



## Review

## Analytical methods for dating modern writing instrument inks on paper

Magdalena Ezcurra<sup>a,\*</sup>, Juan M.G. Góngora<sup>a</sup>, Itxaso Maguregui<sup>b</sup>, Rosa Alonso<sup>a</sup><sup>a</sup> Analytical Chemistry Department, Faculty of Science and Technology, University of Basque Country (UPV-EHU), P.O. Box 644, 48080 Bilbao, Spain<sup>b</sup> Paint Department, Faculty of Fine Arts, University of Basque Country (UPV-EHU), P.O. Box. 644, 48080 Bilbao, Spain

## ARTICLE INFO

## Article history:

Received 6 March 2009

Received in revised form 16 November 2009

Accepted 18 November 2009

Available online 12 January 2010

## Keywords:

Forensic science

Document examination

Questioned documents

Ink

Dating

Relative age

Absolute age

Ball point pen

Roller ball pen

Gel ink pen

## ABSTRACT

This work reviews the different analytical methods that have been proposed in the field of forensic dating of inks from different modern writing instruments. The reported works have been classified according to the writing instrument studied and the ink component analyzed in relation to aging. The study, done chronologically, shows the advances experienced in the ink dating field in the last decades.

© 2009 Elsevier Ireland Ltd. All rights reserved.

## Contents

1. Introduction	2
2. Basic concepts	3
2.1. Closed and open systems	3
2.2. Static and dynamic profiles	3
2.3. Relative and absolute age	3
2.4. Mass invariance	4
3. Background	4
3.1. Mitchell	4
3.2. Soderman and O'Connell	4
3.3. 1959, 1960, 1963—Kikuchi	4
3.4. Sen and Ghosh	4
4. Ball point pen ink dating	5
4.1. Composition of ball point pen inks	5
4.2. Aging ink evaluation	5
4.3. Methods of ink age evaluation based on the evolution of resins over time	5
4.3.1. 1980—Cantú and Brunelle	7
4.3.2. 1987—Cantú and Prough	7
4.3.3. 1987, 1989—Brunelle, Breedlove, Midkiff and Brunelle, Lee	8
4.3.4. 1990—Isaacs and Clayton	8
4.3.5. 1993, 1994—Aginsky	8
4.3.6. 1995—Brunelle	9
4.3.7. 2005–2006 Kirsch, Weyermann, Koehler, Spengler	9

\* Corresponding author. Tel.: +34 94 601 2686; fax: +34 94 601 3500.

E-mail address: [qmeg@telefonica.net](mailto:qmeg@telefonica.net) (M. Ezcurra).

4.4.	Methods of ink age evaluation based on the study of volatile compounds . . . . .	9
4.4.1.	1982—Stewart . . . . .	9
4.4.2.	1985—Humecki . . . . .	10
4.4.3.	1988—Cantú. . . . .	10
4.4.4.	1993, 1994, 1997 Aginsky. . . . .	10
4.4.5.	2000—Brazeau and Gaudreau . . . . .	11
4.4.6.	2002—Brazeau and Gaudreau . . . . .	11
4.4.7.	2004—Locicirio, Dujourdy, Mazzella, Margot, Lock . . . . .	12
4.4.8.	2005—Bügler, Buchner and Dallmayer . . . . .	12
4.4.9.	2007—Weyermann, Kirsch, Costa Vera, Spengler. . . . .	13
4.4.10.	2008—Weyermann, Spengler . . . . .	13
4.5.	Methods of ink aging evaluation based on the variations observed in the dyes . . . . .	13
4.5.1.	1993, 1995—Aginsky . . . . .	13
4.5.2.	2001—Lyter, McKeonwn . . . . .	14
4.5.3.	2001—Grim, Siegel, Allison . . . . .	14
4.5.4.	2001, 2002—Andrasko . . . . .	14
4.5.5.	2005—Andrasko, Kunicki. . . . .	15
4.5.6.	2005—Siegel, Allison, Mohr, Dunn . . . . .	15
4.5.7.	2006—Weyermann, Kirsch, Costa-Vera, Spengler. . . . .	15
5.	Gel ink dating . . . . .	16
5.1.	Composition of gel ink pens. . . . .	16
5.2.	Gel ink dating . . . . .	16
5.2.1.	Study of the degradation of blue gel ink dyes by IP-HPLC and electrospray sequential ionization–mass spectrometry (ESI-MS/MS) . . . . .	16
5.2.2.	Dating black ink strokes of roller ball and gel by GC and UV–vis spectrophotometry [56]. . . . .	17
5.2.3.	Classification and dating of black gel inks by Ion-Pairing High-Performance Liquid Chromatography (IP-HPLC) . . . . .	17
6.	Conclusion . . . . .	18
	Acknowledgements . . . . .	19
	References . . . . .	19

## 1. Introduction

Document dating and, therefore, the time that a document and/or ink could have been once placed on the paper, is one of the most difficult and hardest problems to solve in forensic science. This is mainly due to the great variety of inks that exist on the market, the complexity of chemical processes that inks undergo from the time they are entered on the paper when they begin their aging process and the amount of external factors that can influence this aging process (environmental factors: light, humidity, temperature; in short, storage conditions of the document) [1].

In spite of the complexity of the issue, important advances have been made with the single objective of determining for how long the ink has been deposited on the paper, which would lead to establishing the date on which the document was produced.

The modern writing instruments, Table 1 – those we can find nowadays in any store of any country and, therefore, those that are most frequently used in questioned documents – are divided into two fundamental groups [2]:

1. Ball point pens: Containing oil-based inks and whose colorants are dyes.
2. Non ball point pens: Containing water-based inks and whose colorants are dyes as well as pigments (one, the other or both). In this second group fountain pens, roller ball pens, as well as markers and gel ink instruments are included.

**Table 1**  
Relevant introduction dates into the market in the field of “modern” writing instruments.

Year	Event
1945	Ball point pen.
1950	Glycols as inks' solvents.
1955	Copper Phthalocyanine as a new dye in inks.
1963	Felt tip pens.
1967	Roller ball pens.
1970	Highlighters.
1984	Gel ink pens.

If a study of the ink-aging processes is intended, the elements involved and the physical–chemical processes that these undergo after depositing the ink on the paper, should also be known. In a general and simple manner, it is possible to say that the inks of manual writing instruments are composed of a colorant or mixture of colorants, and a carrier or vehicle with one or several solvents and one or several resins [3].

- Colorants are divided into dyes (soluble in the vehicle and used in viscous and fluid inks) and pigments (dispersed in the vehicle and used, in certain cases, in fluid inks in addition to dyes).
- The vehicle contains a solvent or mixture of them (fast drying organic solvents, water).
- One or several resins that contribute to the properties of the inks, such as the viscosity or adhesion of the ink to the paper.
- Other components are also added in a smaller proportion in order to modify the rheological properties of inks. These additives are usually kept secret by the manufacturing industry.
- In addition to this basic composition a chemical marker system which is no longer in use because of its high cost, was implemented in the 70 s by the Office of Alcohol, Tobacco and Firearms of the American Treasury Department.
- Manufacturers included a tag (chemical marker as rare earth organometallic compounds and traces of optical whiteners) [4–6] which did not vary over time, and another tag that varied yearly. The identification of one or both of these markers can lead forensic scientists to define the earliest possible date of the studied document. On the other hand, this labeling system would undoubtedly imply the need for knowing which manufacturer used which chemical marker.

The aim of this work is to carry out a chronological review of the different analytical methodologies used for ink dating. The review of papers and technical contributions on the professional meetings begins with the marketing of the first ball point pen back in 1945 and goes on until nowadays.

Download English Version:

<https://daneshyari.com/en/article/97096>

Download Persian Version:

<https://daneshyari.com/article/97096>

[Daneshyari.com](https://daneshyari.com)